ACS Macro Letters

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Zwitterionic Alternating Polymerization to Generate Semicrystalline and Recyclable Cyclic Polythiourethanes

Dawei Tan,[‖] Xin Hu,[‖] Zheng Cao, Ming Luo,* and Donald J. Darensbourg*

Cite This: *ACS Macro Lett.* 2020, 9, 866–871

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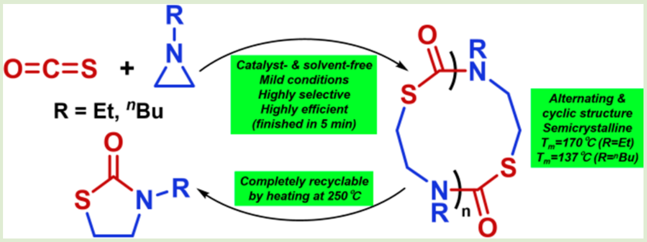
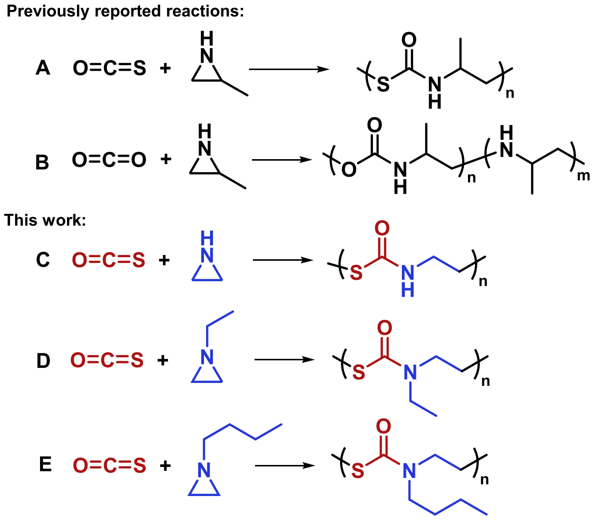
ABSTRACT: Synthesis of cyclic, semicrystalline, and recyclable polythiourethanes was realized via the catalyst-free zwitterionic alternating copolymerization of *N*-alkyl aziridines with carbonyl sulfide (COS) under mild conditions. The copolymerization proceeded efficiently at room temperature and generated copolymers with fully alternating linkages in more than 99% selectivity in 5 min under solvent-free conditions. Notably, the copolymers are typical semicrystalline thermoplastics with melting temperatures up to 137 °C (*n*-butyl-substituted) or 170 °C (ethyl-substituted). The resulting polythiourethanes are predominantly cyclic as evidenced by ^{1}H NMR and MALDI-TOF mass spectroscopies. Remarkably, the cyclic copolymers could be recycled into N-substituted cyclic thiourethanes in quantitative yield by heating at 250 °C for 2 h.

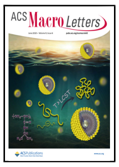


Scheme 1. Copolymerization Systems of Aziridines and COS (CO_2)



The past decades have seen a rapid rise in research dealing with the synthesis of cyclic polymers. Cyclic polymers differ from their linear counterparts by only one bond, yet they exhibit unique properties that vary from linear polymers, including significant differences in lower intrinsic viscosities,[1] smaller hydrodynamic volumes,[2] higher glass transition temperatures,[3] special surface structures,[4] and biological properties in vivo.[5] Zwitterionic ring-opening polymerization (ZROP) is among the most efficient methods for synthesizing cyclic polymers.[6−14] Various nucleophiles such as pyridines,[6] amidines,[7] and N-heterocyclic carbenes (NHCs)[8] have been employed as catalysts in ZROP of lactides,[9] lactones,[10] cyclic siloxanes,[11] and cyclic carbonates.[12] Waymouth et al. have described recent progress in the application and mechanism of ZROP in their review article.[13] Apparently, most of the reported ZROP systems merely involved the homopolymerization of single-component monomers.[9−13] Very recently, we reported a quite different zwitterionic alternating polymerization (ZAP) of two-component monomers generating a cyclic polymer.[14] In that work, a cyclic polythiourethane with alternating structure was synthesized from the spontaneous copolymerization of carbonyl sulfide (COS) and 2-methyl aziridine (MeAz) without any catalysts (Scheme 1A). The proposed mechanism of ZAP and ZROP and their difference are shown and discussed in Scheme S1. In ZAP, M_N and M_E are monomers and catalysts at the same time, and their interactions promote the formation of macromolecular zwitterions and, finally, cyclic polymers. Therefore, this copolymerization is catalyst-free from a macroscopic view. The COS−MeAz copolymerization system exhibited excellent activity and high regioselectivity to produce a cyclic polythiourethane (cPTU) with alternating structure.[14] However, the resulting copolymer was amorphous and possessed a T_g of 90 °C, thus it lacked good thermal deformation resistance. Structure regularity is the primary cause of polymer

Received: April 17, 2020
Accepted: May 27, 2020
Published: May 29, 2020



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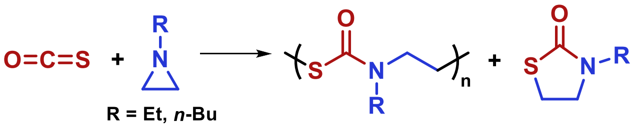
https://dx.doi.org/10.1021/acsmacrolett.0c00302

Table 1. Copolymerization of COS and *N*-Substituted Aziridines



entry[a]	solvent	aziridine	*T* (°C)	time (min)	yield (%)	copolymer selectivity[b] (%)	M_w[c] (g/mol)	$Đ$[c] (M_w/M_n)	T_m (°C)
1	--	^{n}BuAz	20	5	95	>99	3500	1.21	137
2	DMF	^{n}BuAz	20	30	83	>99	5800	2.64	--
3	THF	^{n}BuAz	20	30	88	>99	3200	1.81	--
4	DCM	^{n}BuAz	20	30	89	>99	3300	1.69	--
5	toluene	^{n}BuAz	20	30	85	>99	3100	1.19	--
6	pyridine	^{n}BuAz	20	30	81	>99	3000	1.25	--
7	ethanol	^{n}BuAz	20	30	82	>99	2800	1.26	--
8	H_2O	^{n}BuAz	20	30	85	>99	2900	1.25	--
9	TCE	^{n}BuAz	20	30	79	>99	2900	1.25	--
10	TCE	^{n}BuAz	60	30	78	94	2700	1.23	--
11	TCE	^{n}BuAz	100	30	76	91	2800	1.22	--
12	--	EtAz	20	5	96	>99	19300	1.69	170
13[d]	--	EtAz	20	30	91	>99	2900	1.48	--

[a] Copolymerizations were conducted in a dried 10 mL autoclave with 0.3 mL of aziridine added and a COS/aziridine of 2:1 (molar ratio) at set temperatures. All the conversions of aziridine monomers were >99% based on ^{1}H NMR spectroscopy. [b] The copolymer selectivity represents the molar percentage of the copolymer in total crude product and calculated based on ^{1}H NMR (please see Supporting Information for detailed calculation). [c] M_w and $Đ$ were determined by SEC in THF eluent. Entry 12 was measured by high-temperature SEC with trichlorobenzene as eluent. [d] This reaction was carried out at 1 atm of COS.

crystallization, which significantly improves the polymer's thermal properties.[15−20] Our goal is to design a catalyst-free polymerization system to achieve cyclic and semicrystalline polymers with very regular structures through the ZAP of COS and aziridine compounds. COS has proven to be an excellent building block for synthesizing sulfur-containing polymers.[21−35] It has been chosen as one monomer because it is nucleophilic and less acidic. Comonomer's acidity is an important factor affecting the alternating property in aziridine-involved copolymerization systems. For instance, more acidic CO_2 has been reported to cause inevitable aziridine homopolymerization in CO_2/aziridine copolymerizations (Scheme 1B), affording random and irregular linkages.[36−38] For optimizing aziridine monomers, first unsubstituted aziridine (Az) was tried (Scheme 1C); however, inevitable Az homopolymerization generated defective amine microstructures, and the alternating enchainment was not satisfactory. Furthermore, strong hydrogen bonding of this Az-based copolymer resulted in poor solubility in common solvents such as alcohol, halohydrocarbon, THF, DMF, and DMSO, making characterization very difficult. Subsequently, less nucleophilic *N*-alkyl aziridines were investigated. *N*-Ethyl aziridine (EtAz) was examined (Scheme 1D), and as we anticipated, the substituent ethyl group enhanced the alternating selectivity; however, the copolymer's solubility was still unsatisfactory because of its crystallization. Upon replacing the ethyl group with a more soluble *n*-butyl group, *N*-*n*-butyl aziridine (^{n}BuAz), the resulting copolymer exhibited crystallizability and meanwhile relatively good solubility in common solvents. Therefore, ^{n}BuAz was chosen as the model monomer for copolymerization with COS (Scheme 1E). Herein, we have developed a mild, catalyst-free, and very active ZAP of COS and *N*-alkyl aziridines to provide cyclic and semicrystalline polythiourethanes with alternating structures. Furthermore, the cyclic copolymers could be recycled into corresponding *N*-alkyl cyclic thiourethanes (cTUs) upon heating at 250 °C for 2 h.

We initially carried out the reaction under solvent-free conditions at 20 °C in order to examine the activity of the spontaneous copolymerization of COS and ^{n}BuAz (entry 1, Table 1). ^{n}BuAz was completely converted in 5 min to the corresponding *N*-*n*-butyl polythiourethane (^{n}Bu-cPTU) with a molecular weight (MW) of 3500 g/mol and a dispersity of 1.21. The copolymer selectivity was >99% based on the ^{1}H NMR spectrum of the crude product (Figure S3). This represents an excellent example of the highly selective and catalyst-free synthesis of N-substituted polythiourethane from COS and *N*-alkyl aziridine. Hence, the influence of solvents on this process was investigated, and the results are summarized in Table 1. The reaction time was set at 30 min to ensure complete conversion of ^{n}BuAz. The polar solvent DMF exhibited a small increase in the polymer's molecular weight, but it resulted in a slightly broader dispersity (entry 2, Table 1). The molecular weight decreased slightly when some common solvents were used (entries 3−6, Table 1) in comparison with solvent-free conditions. It is worth noting that water and ethanol did not suppress the copolymerization or significantly decrease the molecular weight when used as solvents (entries 7 and 8), although they are widely used as chain transfer agents in many polymerization systems.[1,21,29] This COS/^{n}BuAz copolymerization exhibited much higher activity and stronger solvent-tolerant property than our previously reported COS/MeAz copolymerization system,[14] which is embodied in shorter reaction time and less sensitive molecular weight and copolymer selectivity. Subsequently, we investigated the effects of reaction temperature on the polymerization process. 1,1,2,2-Tetrachloroethane (TCE) was used as solvent because of its high boiling point (147 °C) and good dissolving capacity for these copolymers. Upon increasing the reaction temperature from 20 to 60 and 100 °C (entries 10 and 11), the copolymer selectivity decreased from >99% to 94% and 91%, respectively, with a slight decrease and fluctuation of molecular weights. The generation of more five-membered ring cyclic thiourethanes indicated that the copolymer selectivity slightly decreased at higher temperatures, but it still maintained a high value (91%) even at relatively high temperature (100 °C). Therefore, 20 °C and solvent-free conditions were the optimum reaction conditions for this copolymerization process. EtAz was more active than ^{n}BuAz, being fully converted in 5 min at 20 °C in the copolymerization with COS providing an *N*-ethyl polythiourethane (Et-cPTU) with a M_w of 19.3 kg/mol (entry 12, Table 1), which was much higher than that of ^{n}Bu-cPTU, resulting from the same conditions. The molecular weight characteristics were determined by high-temperature SEC with trichlorobenzene as eluent because the resulting Et-cPTU was only soluble in TCE or trichlorobenzene upon heating above 130 °C. However, the ^{n}Bu-cPTU analogue was soluble in many common solvents such as DCM, chloroform, THF, and DMF at room temperature or upon slight heating. We consider that more liposoluble *n*-butyl substituent groups and smaller molecular weights resulted in the better solubility of ^{n}Bu-cPTU than Et-cPTU.

The alternating and cyclic structures of the resulting polythiourethanes were inferred by ^{1}H NMR spectrometry and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. In the ^{1}H NMR spectrum (Figure S4) of ^{n}Bu-cPTU, the chemical shifts were all clearly assigned to the protons of ^{n}Bu-cPTU. All NMR signals were assigned with the integration ratio being in accord with the protons' molar ratio. There were no observable signals for polymer end groups, five-membered ring cyclic thiourethanes, or imine linkages.[38] In addition, all the chemical shifts were clearly assigned in ^{13}C NMR (Figure S5). The MALDI-TOF mass spectrum of ^{n}Bu-cPTU (entry 1, Table 1) shows molecular ions attributed to the sodium adducts of ^{n}Bu-cPTU (Figure 1A). Figure 1B presents a group of equidistant peaks revealing one population of macromolecules separated by 159.07 mass units, which corresponds to ^{n}Bu-cPTU with alternating thiourethane linkages and one extra imine linkage. This structural composition is consistent with our reported COS/MeAz system's result.[14] Figure 1C shows a zoomed and very clear high-resolution spectrum of the peak at 4257.4 *m*/*z*, demonstrating the accuracy of this assignment. Furthermore, the copolymerization of COS and EtAz was carried out at only 1 atm of COS (entry 13, Table 1) to generate low molecular weight Et-cPTU (M_w = 2900 g/mol, $Đ$ = 1.48) in order to improve its solubility. Analysis of the resulting Et-cPTU by MALDI-TOF mass spectrometry (Figure S34) revealed ions corresponding to cyclic Et-cPTU with an alternating structure. Hence, the copolymerization of COS and *N*-alkyl aziridines has been shown to be an efficient strategy for synthesizing cyclic and alternating polythiourethanes.

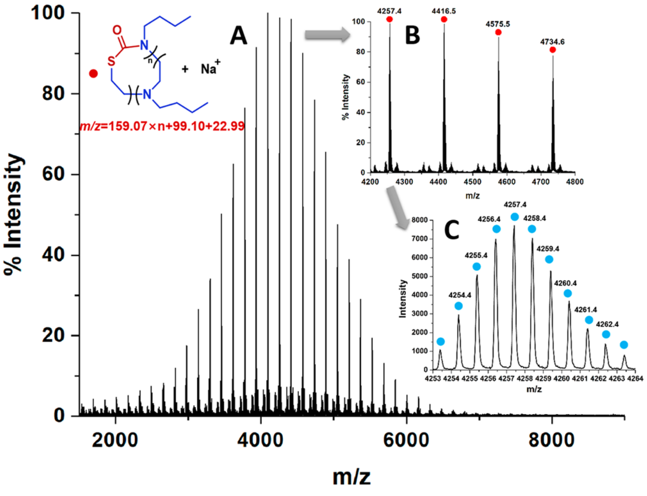


Figure 1. MALDI-TOF MS spectrum of ^{n}Bu-cPTU (entry 1, Table 1).

The thermal properties of ^{n}Bu-cPTU were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the curves are shown in Figures S28 and S30. As anticipated, the structure-regular copolymer was found to be a typical semicrystalline material with a melting endothermic peak at 137 °C and a crystalline exothermic peak at 88 °C. No T_g was observed by DSC for this copolymer. The crystallizability of ^{n}Bu-cPTU was further confirmed by powder X-ray diffraction (XRD) (Figure S32). Evident sharp diffraction peaks were observed, demonstrating its semicrystalline structure. ^{n}Bu-cPTU displayed an initial decomposition temperature at 5% weight loss ($T_{d,5\%}$) of 248 °C measured under a nitrogen atmosphere (Figure S28), indicating that this copolymer possesses good thermal stability. The DSC and XRD characterizations of Et-cPTU are shown as Figures S31 and S33, demonstrating Et-cPTU is also a semicrystalline polymer, and it had a melting point (T_m) of 170 °C. These results demonstrate that the thermal resistance of these polythiourethanes was enhanced by their crystallizability compared to the amorphous COS/MeAz copolymer.

We speculate that these *N*-alkyl polythiourethanes might possess thermal recyclability similar to the COS/MeAz copolymer.[14] The thermal recyclability of these polythiourethanes was examined by heating at 200 °C and 250 °C for 2 h in sealed tubes (Table S1). After cooling, light yellow liquid products were obtained and confirmed to be corresponding to *N*-alkyl cTUs by NMR (Figures S20−S23) and liquid chromatography−mass spectrometry (LC-MS) (Figures S35 and S36). Figure 2 reveals the conversion of ^{n}Bu-cPTU into ^{n}Bu-cTU after thermal decomposition, as evidenced by the disappearance of the chemical shift characteristics of ^{n}Bu-cPTU and the appearance of the chemical shift characteristics

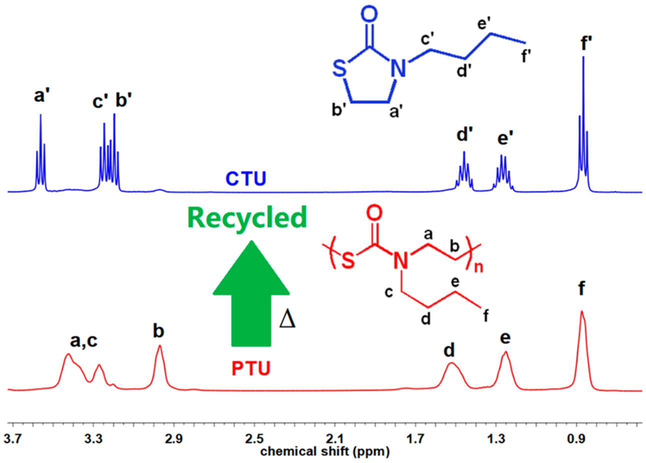
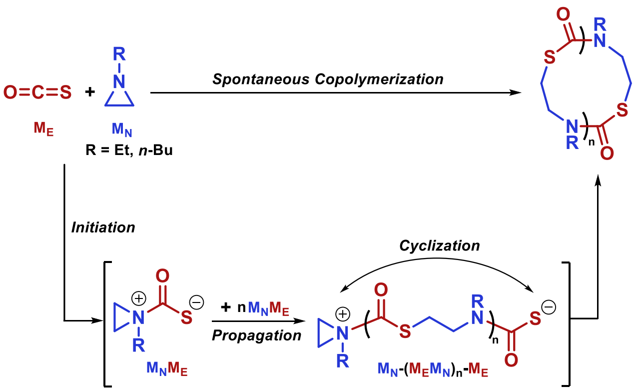


Figure 2. Thermal recyclability of ^{n}Bu-cPTU. Top: The liquid product obtained after thermal degradation at 250 °C for 2 h. Bottom: ^{1}H NMR spectra ($CDCl_3$) of ^{n}Bu-cPTU (entry 1, Table 1).

of ^{n}Bu-cTU. Et-cPTU also underwent a similar thermal recycle by completely depolymerizing into Et-cTU upon heating at 250 °C for 2 h (Figure S27). Cyclic thiourethanes, also known as thiazolidin-2-ones, are important building blocks in both pharmaceutical and synthetic organic chemistry.[39] Therefore, these polythiourethanes can be completely recycled by thermally depolymerizing into valuable small molecules. The whole process of the copolymerization and depolymerization of COS and *N*-alkyl aziridines is sustainable and atom-economical.

This facile COS/*N*-alkyl aziridine copolymerization and the generation of cyclic polythiourethanes are proposed to proceed via the aforementioned ZAP mechanism (Scheme 2). Nucleophilic attack of the *N*-alkyl aziridines (M_N) at COS (M_E) would generate zwitterionic intermediates (M_NM_E) which can copolymerize with other zwitterionic intermediates to propagate. At last, chain cyclization occurred via intramolecular backbiting to yield cyclic polythiourethanes. To our knowledge, there are no other reported well-defined semicrystalline and cyclic polythiourethanes with alternating structures.

Scheme 2. Plausible Mechanism of ZAP of COS and *N*-Alkyl Aziridines



Attempts to generate and isolate a zwitterionic intermediate have to date been unsuccessful. Therefore, we have carried out DFT calculations to assess the energies of the likely intermediates (Figure 3). Optimized structures and relative enthalpies at 0.00 K were calculated using Gaussian 09[40] at the M06[41]/6-311G+(d,p) level of theory (see Supporting Information for computational details) under solvent-free conditions. The enthalpies are referenced to ^{n}BuAz and COS at infinite separation at 0.00 K. DFT calculations reveal one low-energy intermediate, the zwitterion M_NM_E, for which local minima could be located at $\Delta H_{0.00}$ = 27.9 kcal/mol. Hence, we propose that the zwitterions are the active species mediating chain growth. We also carried out DFT calculations to assess the energies of the formation of the five-membered ring cyclic thiourethane (Figure S52), and the calculation revealed the formation of cyclic thiourethane needs to overcome a much higher barrier (97.53 kcal/mol) than that (51.69 kcal/mol) of polymer product.

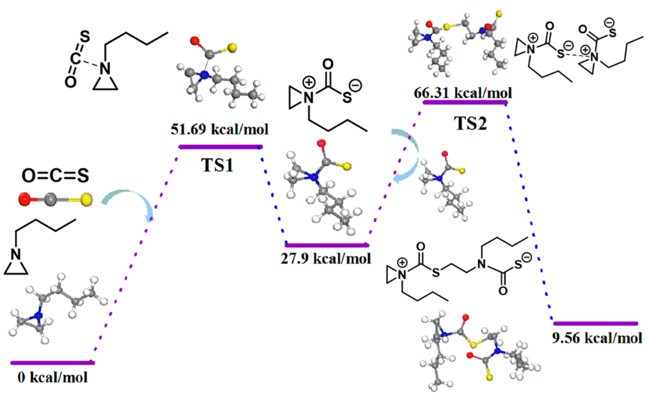


Figure 3. DFT computed enthalpy for intermediates M_NM_E and $M_NM_EM_NM_E$ with respect to free COS and ^{n}BuAz.

In summary, the catalyst-free alternating copolymerization of COS and *N*-alkyl aziridines occurs readily at room temperature and under solvent-free conditions to afford well-defined cyclic and semicrystalline polythiourethanes with alternating structures. These results illustrate the effectiveness of ZAP for generating cyclic macromolecules. Furthermore, these polythiourethanes were shown to be recyclable to cyclic thiourethanes upon heating. Future work will explore the scope of monomers which could copolymerize via ZAP to provide versatile cyclic polymers, as well as catalytic systems which could promote ZAP to achieve cyclic polymers with good controllability. Meanwhile, the ring-opening polymerization of the resulting cyclic thiourethanes to reproduce polythiourethanes is currently under investigation in an effort to provide a closed-loop approach toward a circular materials economy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00302.

> NMR and MALDI-TOF mass spectra; SEC, DSC, and XRD curves of the copolymers; and NMR and LC-MS spectra of the cyclic products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Ming Luo − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China;* orcid.org/0000-0002-6166-0681; Email: tianyaguzhao@zju.edu.cn

Donald J. Darensbourg − *Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States;* orcid.org/0000-0001-9285-4895; Email: djdarens@chem.tamu.edu

Authors

Dawei Tan − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China*

Xin Hu − *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China;* orcid.org/0000-0001-8113-8631

Zheng Cao − *Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou, Jiangsu 213164, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmacrolett.0c00302

Author Contributions

[‖]D.W.T. and X.H. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.W.T. and X.H. contributed equally to this work. We acknowledge support from the Natural Science Foundation of China (21704007), Natural Science Foundation of Jiangsu Province (BK20170434), the National Science Foundation (CHE-1665258), and the Robert A. Welch Foundation (A-0923).

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